Commonwealth of Kentucky
Division for Air Quality

RESPONSE TO COMMENTS

Title V, Operating
Permit: V-07-008
Air Products and Chemicals, Inc.
Catlettsburg, KY 41129
Date: August 28, 2007
Sukhendu K. Majumdar, Reviewer

SOURCE ID:	21-019-00117
SOURCE A.I. #:	83915
ACTIVITY ID:	APE20070001

SOURCE DESCRIPTION:

The hydrogen plant, which is owned and operated by Air Products and Chemicals, Inc., provides "over the fence" hydrogen and steam to the Catlettsburg Refinery. Construction and operation of the hydrogen plant was authorized by the Division for Air Quality in the permit VF-02-001, which was issued to Catlettsburg Refining, LLC. Since the hydrogen plant is owned and operated by Air Products and Chemicals, Inc., both the source and Catlettsburg Refining, LLC prefer that the hydrogen plant be issued a separate Title V permit.

The hydrogen plant, operated by Air Products, produces hydrogen using steam methane reforming technology to supply hydrogen and steam to the Marathon Petroleum Company's Catlettsburg petroleum refinery. Natural gas is the methane source. Natural gas process feed and recycled hydrogen product are compressed, and then directed to the hydrogenation and desulfurization beds, where hydrogenation and desulfurization occur to remove sulfur from natural gas to prevent poisoning of the reformer catalyst. The desulfurization beds contain zinc oxide catalyst to adsorb any sulfur compound to form zinc sulfide. When the catalyst becomes spent, it is removed and disposed of. Steam is mixed with the desulfurized gas and the mix is directed to the reformer.

The reformer contains catalyst filled tubes in which reactions occur. The mixed feed is converted into hydrogen and a mixture of carbon oxides. The syngas effluent from the reformer tubes is cooled and enters the high temperature shift reactor where any CO in the gas is converted to CO2 and additional hydrogen. The syngas out of the reactor is purified in the multi-vessel pressure swing adsorption unit where the impurities are adsorbed allowing high purity hydrogen to pass through. The hydrogen plant uses a flare to burn excess hydrogen product during the refinery hydrogen demand curtailment and also to burn PSA feed gas (syngas), PSA purge gas, hydrogen product, natural gas, relief valve vents from hydrogen plant during the startup, shutdowns, process upsets, malfunction, maintenance and emergencies.

SINGLE SOURCE DETERMINATION:

The hydrogen plant, operated by Air Products, produces hydrogen using steam methane reforming technology to supply hydrogen and steam only to the Marathon Petroleum Company's Catlettsburg petroleum refinery. Marathon Petroleum Company's Catlettsburg refinery is a PSD major source for regulated pollutants. Air Products' hydrogen plant is within the property limit of Marathon's refinery. Together they are considered by the Kentucky Division for Air Quality to be a single

"major source" as defined in 401 KAR 52:001, Section (1)(45)(b), definition of Major source for regulated air pollutants other than HAPS. Each owner/operator is responsible and liable for their own violations unless there is a joint cause for the violations.

PUBLIC AND U.S. EPA REVIEW:

The affected states (Ohio and West Virginia) were notified of the issuance of the draft permit on June 25, 2007, via e-mail. On July 2, 2007 the public notice on availability of the draft permit and supporting material for comments by persons affected by the plant was published in *The Ashland Independent*, Ashland, Kentucky. The public comment period expired 30 days from the date of publication.

Comments were received from Air Products and Chemicals, Inc., on July 31, 2007. Comments and response to comments are attached in Attachment A. Changes as necessary were made to the proposed permit as a result of the comments received, however the Division has concluded that the proposed operation will comply with all air quality regulations and requirements. Therefore, the Division has made a final determination to issue a proposed permit. The proposed permit will become final upon approval of the EPA.

ATTACHMENT A

Response to Comments

Comments on Air Products and Chemicals, Inc. Catlettsburg Hydrogen Plant Draft Title V Air Quality Permit submitted by Mr. Kent S. Kisenbauer, Environmental Engineer for Air Products and Chemicals, Inc.

Permit Application Summary Form

1. Permit Application Summary Form, Page 2 of 3, Emissions Summary

Potential source-wide total NOx emissions in the summary table are not consistent with the source-wide emissions cap contained in Section D's Compliance Demonstration Method of the permit. The emissions summary table source-wide NOx PTE is 128.9 ton/yr, while the Section D source-wide NOx limit is 112.7 ton/yr. Please revise the emissions summary table to reflect the permitted source-wide NOx PTE of 112.7 ton/yr.

Division's response: Comment acknowledged, change made.

2. Permit Application Summary Form, Page 2 of 3, Source Description, 3rd Paragraph, Last Sentence

The description should be revised to clarify that the flare burns other process gases besides hydrogen product. (Refer to page 2-3 of the January 31, 2007 permit application for a description of the other gases burned in the flare.) Please change the description to:

"The hydrogen plant uses a flare to burn excess hydrogen product during refinery hydrogen demand curtailment and also to burn PSA feed gas (syngas), PSA purge gas, hydrogen product, natural gas, and relief valve vents from the hydrogen plant during startups, shutdowns, malfunctions, process upsets, maintenance, and emergencies."

Division's response: Comment acknowledged and changes were made to better describe flare gases.

3. Permit Application Summary Form, Page 3 of 3, List of Emission Points

Emission Point EP-03 should be called simply a "Flare", rather than an "Emergency Vent Flare". The flare is used at other times besides emergencies.

Division's response: Comment acknowledged, change made.

4. Permit Application Summary Form, Page 3 of 3, Single Source Determination

Same comment as #11 below regarding the hydrogen plant's relationship with the Catlettsburg Refinery.

Division's response: Refer to the response to comment# 11.

5. Permit Application Summary Form, Page 3 of 3, Emissions and Operating Caps Descriptions

In Emissions and Operating Cap descriptions "None" is shown. There are source-wide emission caps as evidenced by Section D's Compliance Demonstration Method of the permit. So please change this description accordingly.

Division's response: Source-wide emission limits for NOx, CO and VOC are added under the emissions and operating cap description.

Permit Statement of Basis

6. Permit Statement of Basis, Page 1 of 4, Source Description, 3rd Paragraph, Last Sentence

Same comment as #2 above regarding the gases burned in the flare.

Division's response: Comment acknowledged, change made.

7. Permit Statement of Basis, Page 1 of 4, List of Emission Points

Same comment as #3 above regarding our request to change the flare description from "Emergency Vent Flare" to simply "Flare."

Division's response: Comment acknowledged, change made.

8. Permit Statement of Basis, Page 2 of 4, Single Source Determination

Same comment as #11 below regarding the hydrogen plant's relationship with the Catlettsburg Refinery.

Division's response: Refer to the response to comment# 11.

9. Permit Statement of Basis, Page 2 of 4, Table 1 Emissions Summary

Potential NOx emissions from EP-01 are not consistent with emission rates given in the permit application. This results in a source-wide potential NOx emission rate that does not match the source-wide emissions cap contained in Section D's Compliance Demonstration Method of the permit. The Section D source-wide limit is 112.7 ton/yr NOx, whereas the table gives a total NOx of 128.86 ton/yr. Please add a comment below the emissions summary table noting that there are source-wide emission limits that differ from and over-ride the emission rates given in the table.

For the statement regarding emission points EP-03, EP-04, and EP-05 above Table 1, please delete the mention of stack test results. Stack test results are not relevant to the flare, plant-wide fugitive emissions, and plant-wide intermittent and continuous steam vents.

Division's response: Comment acknowledged, change made.

10. Permit Statement of Basis, Page 3 of 4, Non-Applicable Regulations

In the 5th paragraph, the regulatory citation needs to be corrected. Please change the wording of this paragraph to read:

"401 KAR 60:005, incorporating by reference 40 CFR 60 Subpart VV – Standards of Performance for Equipment Leaks of VOC in the SOCMI, does not apply.

The following paragraph should be added:

"401 KAR 60:005, incorporating by reference 40 CFR 60 Subpart GGG – Standards of Performance for Equipment Leaks of VOC in Petroleum Refineries, does not apply."

Division's response: Comment acknowledged, change made.

Title V Permit Section

11. Permit Section A, Page 1 of 27, Permit Authorization, Single Source Determination

Air Products would like to reinforce/clarify the basics of our hydrogen plant's relationship with the Catlettsburg Refinery. The hydrogen plant is located on the Refinery property. However, as indicated in our January 31, 2007 application, the SIC Code of the hydrogen plant is 2813, "Industrial Gases," not 2911, "Petroleum Refining." The cover page of the Division's "Preliminary Permit Determination" and the "Permit Application Summary Form" properly show "Industrial Gases" and "SIC code: 2813" for the hydrogen plant. The hydrogen plant is owned and operated by Air Products (as properly indicated in the first paragraph of the "Source Description" of the draft permit's Application Summary Form). Air Products employees manage and operate the hydrogen plant. Air Products sets the budget for the hydrogen plant. Air Products sells the hydrogen plant's products to the Refinery under a sale-of-gas contract. Air Products makes and funds the capital/maintenance decisions for the hydrogen plant. Therefore, we do not meet the second and third prongs (b.2 and b.3) of the four-prong test in the definition of "major source" for regulated pollutants other than HAPs as defined in 401 KAR 52:001, Section (1)(45)(b).

Division's response: The Marathon Petroleum Company's Catlettsburg refinery is a major source for HAPs. Referring to 401 KAR 52:001 Section (1)(45)(a), the conditions are met for a single source determination. If there are contractual agreements between Air Products and Chemicals, Inc. and the Catlettsburg Refining Company, then it becomes a common control. If over fifty (50) percent of the hydrogen generated at the facility is used at the Catlettsburg Refinery, then EPA would refer to Air Products and Chemicals' Hydrogen Plant as a support facility for the refinery. Support facilities are considered to be part of the same industrial grouping as that of the primary facility it supports, even if the support facility has a different four digit SIC code. Therefore, the conditions for a single source determination is met by 401 KAR 52:001 Section (1)(45)(b) also.

12. Permit Section B, Page 2 of 27, Hydrogen Reformer, Description, 1st Paragraph

For a more accurate description of the Hydrogen Reformer, please change the first paragraph to:

The steam methane reforming (SMR) process includes a reformer, which contains catalyst-filled tubes. Natural gas is the process feed. The reforming reactions that produce hydrogen occur in the

catalyst-filled tubes. The reformer combusts fuels to generate the necessary heat of reaction. Pressure swing adsorption (PSA) purge gas, natural gas, and reformer synthesis gas (syngas) are the possible fuels. Emissions go out through the hydrogen reformer flue gas stack.

Division's response: Comment acknowledged, change made.

13. Permit Section B, Page 2 of 27, Hydrogen Reformer, Description, Controls

For the Hydrogen Reformer, "Controls" is shown as "None." However, the burner vendor's "Performance Demonstration" reports dated 11/8/02 describe the 65% and 100% burners as, "… down-fired, round flame, combination Natural Gas, PSA Gas burner. As a part of John Zink's InfurNOx^{TM} family of burners, it uses internal flue gas recirculation to reduce the peak flame temperature, which in turn reduces NOx emissions. The burner was designed for natural draft operation."

Division's response: Comment acknowledged, change made.

14. Permit Section B, Page 3 of 27, Hydrogen Reformer, Specific Emission Limitation #2.a

The emission limits are not consistent with the emission rates provided in the January 31, 2007 permit application. Instead, they are a carryover from the individual Hydrogen Reformer Furnace emission limits in Permit Number VF-02-001.

Because there are source-wide emission limits over the entire facility (as specified in Section D's Compliance Demonstration Method of the permit), these individual source emission limits for the reformer furnace are not necessary and should be removed from the permit. Note that this condition is also repeated as Section D, Condition #3.b.

If the Division determines that it needs to retain the individual Hydrogen Reformer emission limits in the permit, they should appear only in Section D of the permit, with the compliance demonstration method specified as compliance with the source-wide daily-calculated rolling 365-day emission limits. In a discussion with the Division on July 11, 2007, the Division clearly stated that Air Products does not need to comply with these individual emission limits in Section B, but rather only the three source-wide emission limits (NOx, CO, and VOC) in Section D's Compliance Demonstration Method (page 16 of 27). See Comment #30 for similar discussion of this matter.

Division's response: The compliance demonstration method for SO2 and PM10 is not included in Section D. Therefore, the original limit from VF-02-001 is included for this unit. The compliance demonstration method has been changed to " The permittee shall calculate for each day, in tons per year, the 365-day rolling sum emissions of SO2 and PM10."

15. Permit Section B, Page 3 of 27, Hydrogen Reformer, Specific Emission Limitation #2.a

The condition limits the reformer furnace heat input to 455 mmBtu/hr. This is the furnace capacity given in the "Description" (on page 2 of 27 of the permit) for this emission unit, so it is not necessary to repeat as an enforceable limit. Please remove this condition. Note that this condition is also repeated as Section D, Condition #3.b.

Division's response: The condition remains in Section D and was in the previous synthetic minor limit in the permit VF-02-001.

16. Permit Section B, Page 4 of 27, Hydrogen Reformer, Compliance Demonstration Method

In light of Comment #14 above, Section B's Compliance Demonstration Method can be deleted in its entirety. The statement about measuring NOx with a CEMS can be moved to Section D's Compliance Demonstration Method. The portions of the statements about how to calculate CO emissions and VOC emissions can be moved to Section D's Compliance Demonstration Method. The portions of the statements about how to calculate SO2 and PM10 emissions can be deleted since Section D's Compliance Demonstration Method does not present source-wide emission limits for SO2 and PM10.

Division's response: Refer to the response to comment# 14 for 2.a. Condition 2.b refers to Section D, which repeats the limit and lists a compliance demonstration method.

17. Permit Section B, Page 4 of 27, Hydrogen Reformer, Specific Testing Requirement #3.b

The condition requires that a CO performance test of the hydrogen reformer furnace be conducted within 180 days of issuance of the final permit. An initial performance test of CO in the Hydrogen Reformer Flue Gas Stack was conducted on April 28, 2004 and the test report was submitted to the Division on June 25, 2004. The average CO emission rate over the three test runs was 0.06 lb/hr, which resulted in a calculated CO emission factor of 0.000161 lb CO/mmBtu heat input. Therefore, we are requesting that this new performance test requirement be deleted.

Division's response: Based on low actual emissions during the 2004 testing, the new performance testing for CO emissions has been deleted. (Previous emission factor was 0.04 lb of CO/mmBtu).

18. Permit Section B, Page 5 of 27, Hydrogen Reformer, Specific Recordkeeping Requirements

It seems appropriate to require records of the results of the H2S alternative monitoring results. Please add the following statement to the permit recordkeeping requirements:

"The Permittee shall retain records of the H2S alternative monitoring plan sampling results."

Division's response: The Division has revised the permit as requested by the source.

19. Permit Section B, Page 5 of 27, Hydrogen Reformer, Specific Recordkeeping Requirements

In light of Comment #15 requesting that the reformer furnace heat input rate limit be deleted, it seems appropriate that Specific Recordkeeping Requirement #5.a can be deleted.

Division's response: Refer to the response to comment# 15.

20. Permit Section B, Page 6 of 27, Hydrogen Reformer, Specific Reporting Requirements

It seems appropriate to make reference to Section D, "Source Emission Limitations and Testing Requirements," like is done on page 8 of 27 under the Specific Reporting Requirements for the

Condensate Stripper Vent. Please add such a reference under the Specific Reporting Requirements on page 6 of 27.

Division's response: The Division has revised the permit as requested by the source.

21. Permit Section B, Page 9 of 27, Flare, Description

The description should be changed to clarify that gases other than hydrogen are flared. See Comment #2. Also, the flare is equipped with two pilots, not just one. Therefore, please change the flare description to:

"The hydrogen plant uses a flare equipped with natural gas-fired pilot burners to burn excess hydrogen product during refinery hydrogen demand curtailment and also to burn PSA feed gas (syngas), PSA purge gas, hydrogen product, natural gas, and relief valve vents from the hydrogen plant during startups, shutdowns, malfunctions, process upsets, maintenance, and emergencies."

For clarification, please change the wording of "Capacity" to:

"Capacity - Natural Gas-fired Pilots: Total of 200 standard cubic feet per hour (nominal)"

Division's response: The Division has revised the permit as requested by the source.

22. Permit Section B, Page 9 of 27, Flare, Specific Emission Limitation #2.a, Compliance Demonstration Method

The Compliance Demonstration Method for Specific Emission Limitation #2.a states that compliance is demonstrated by burning natural gas and hydrogen only. However, it must be noted that the flare also burns process gases derived from the natural gas and water raw material feeds. These process gases are all clean burning, low-carbon content gases. Similar to burning natural gas and hydrogen, burning these process gases should not cause opacity. The text should be changed to read: "Compliance is demonstrated by the combustion of natural gas, hydrogen product, and hydrogen plant process gases only."

Division's response: The Division has revised the permit as requested by the source.

23. Permit Section B, Page 11 of 27, Fugitive Emissions, Non-Applicable Regulations, 4th and 5th Paragraphs

In the 4th and 5th paragraphs, the regulatory citations need to be corrected. Please change the wording of these two paragraphs to read:

"401 KAR 60:005, incorporating by reference 40 CFR 60 Subpart GGG – Standards of Performance for Equipment Leaks of VOC in Petroleum Refineries, does not apply. The hydrogen plant is primarily engaged in manufacturing of industrial gas for sale and is not a petroleum refining process."

"401 KAR 60:005, incorporating by reference 40 CFR 60 Subpart VV – Standards of

Performance for Equipment Leaks of VOC in the SOCMI, does not apply. The hydrogen plant is not a synthetic organic chemical manufacturing process."

Division's response: The Division has revised the permit as requested by the source.

24. Permit Section B, Page 12 of 27, Fugitive Emissions, Specific Recordkeeping Requirements

The condition requires calculations of VOC and CO fugitive equipment leak emissions, and states that "In place of actual emission rates, the permittee **shall** use worst-case emissions" (emphasis added). The facility should not be required to use worst-case emissions only, but should be allowed to use actual emission rates if information is available. The text should be changed to read: "In place of actual emission rates, the permittee **may** use worst-case emission estimates." Such wording would be consistent with that used in Permit Section D, Compliance Demonstration Method #b, page 16 of 27.

Division's response: The Division has revised the permit as requested by the source.

25. Permit Section B, Page 13 of 27, Steam Vents, Specific Recordkeeping Requirements

Similar to Comment #24 above, the text should be changed to read:

"In place of actual emission rates, the permittee **may** use worst-case emission estimates."

Such wording would be consistent with that used in Permit Section D, Compliance Demonstration Method #b, page 16 of 27.

Division's response: The Division has revised the permit as requested by the source.

26. Permit Section C, Page 14 of 27, Insignificant Activities

Item number 1 should be changed to: "Cooling tower (1000 gpm nominal)"

Item number 2 should be changed to the plural ("Analyzer vents") because there is more than one analyzer vent.

Division's response: The Division has revised the permit as requested by the source.

27. Permit Section D, Page 15 of 27, Source Emission Limitations and Testing Requirements, Condition #2

Please confirm that Condition #2 is a boilerplate condition. We just wanted to reinforce/clarify that Section D's Compliance Demonstration Method does not include source-wide emission limits for SO2 and PM10.

Division's response: Comments confirmed. Condition# 2 is a standard condition that lists the pollutants that have an emission limitation in the permit, not just Section D.

28. Permit Section D, Page 15 of 27, Source Emission Limitations and Testing Requirements, Condition #3.a

The condition refers to the "Hydrogen Generation Unit". The name of the emission unit in question is the Condensate Stripper Vent (Emission Unit EP-02). In Permit VF-02-001, the name Hydrogen Generation Unit was applied to the overall Hydrogen Plant and it was stated that the Hydrogen Generation Unit included a "Reformer Vent." In Permit VF-02-001, the emission source label of "Hydrogen Generation Unit (Reformer Vent)" was improperly applied to the Condensate Stripper Vent.

Division's response: Comment noted.

29. Permit Section D, Page 15 of 27, Source Emission Limitations and Testing Requirements, Condition #3.a and #3.b

The emission limits for the "Hydrogen Generation Unit" (actually the Condensate Stripper Vent) and the Hydrogen Reformer Furnace are not consistent with the emission rates provided in the January 31, 2007 permit application.

Because there are source-wide emission limits over the entire facility (see Compliance Demonstration Method #a on page 16 of 27), the individual emission limits for the Condensate Stripper Vent and Hydrogen Reformer Furnace are not necessary and should be removed from the permit. See Comment #30 for additional discussion of this matter.

Condition #3.b limits the reformer furnace heat input to 455 mmBtu/hr, based on a 365-day rolling average. This is the furnace capacity given in the description for this emission unit in Permit Section B, Page 3 of 27, Hydrogen Reformer, Specific Emission Limitation #2.a, so it is not necessary to repeat as an enforceable limit. Please remove this condition. See Comment #15 for similar discussion of this matter.

Division's response: The condition is the same as in the previous permit, VF-02-001.

30. Permit Section D, Page 15 of 27, Source Emission Limitations and Testing Requirements, Condition #3.a and #3.b

If the Division determines that it needs to retain the individual Hydrogen Reformer and Condensate Stripper Vent emission limits in the permit, then Air Products would like confirmation from the Division that exceeding these individual ton/yr emission limits will not be a violation of the permit, since the compliance demonstration method is compliance with the source-wide NOx, CO, and VOC emission limits on page 16 of 27 of Section D of the permit. In other words, Air Products will not be required to demonstrate compliance with the individual ton/yr emission limits on page 15 of 27 of Section B of the permit. This is our understanding based on a discussion with the Division on July 11, 2007. See Comment #14 for similar discussion of this matter.

Division's response: Correct. Refer to the compliance demonstration method in Section B and Section D. Compliance with the NOx, CO, and VOC limit is in Section D.

31. Permit Section D, Page 16 of 27, Source Emission Limitations and Testing Requirements, Compliance Demonstration Method

In Compliance Demonstration Method #a, source-wide emission limits are shown for the pollutants NOx, CO, and VOC. Therefore, the Division is requested to please confirm our understanding that there are not any emission limits (source-wide or individual) for PM10 and SO2.

Based on our comment above for Compliance Demonstration Method #a, it is our understanding that the calculated and recorded emissions referred to in Compliance Demonstration Method #b are only NOx, CO, and VOC, and not PM10 and SO2. The Division is requested to confirm this understanding.

Division's response: Correct. There are only limits and compliance for PM10 and SO2 for the Hydrogen Reformer in Section B, not Section D.

32. Miscellaneous Comment, Request for Implementation Period

Air Products is requesting an implementation period for the final permit. This period will allow us to develop, implement, and function check our compliance plan for the final permit. We are proposing a 90-day implementation period, with the effective date of the final permit occurring ninety (90) days after the issuance date of the final permit to Air Products.

We will need such an implementation period since, based on our review of the draft permit, there will be mainly two significant new aspects to the final permit (as compared to the current Permit Number VF-02-001 that the plant has been and continues to operate under): (1) flare emissions must now be determined; and (2) compliance must now be shown with source-wide emission limits rather than individual source emission limits.

As a result of these likely two new aspects of the final permit, we must make significant changes involving the hydrogen plant's Distributed Control System (DCS) and Continuous Emissions Monitoring System (CEMS). Hardware and possibly software changes must be made in order to send additional signals from the DCS to the CEMS Data Acquisition System (DAS). Even though the existing NOx CEMS is intended to just monitor the reformer flue gas stack, we plan to use the CEMS DAS to manage the emissions data in order to demonstrate compliance with the source-wide, daily-calculated, rolling 365-day sum (total) NOx, CO, and VOC limits of Section D's Compliance Demonstration Method of the new permit. Also, software changes must be made to the CEMS DAS so as to calculate flare emissions, to sum individual source emissions in order to calculate the source-wide emissions, and to prepare the appropriate reports. We would probably need to involve the third party CEMS software supplier in this effort.

During the 90-day implementation period, we would continue to comply with the hydrogen plant portions of Permit Number VF-02-001 (as we are now doing) and make any required certifications to the Division or other regulatory agencies accordingly.

Division's response: The facility will have at least 45 days after the proposed permit is issued. When the permit is final, there is no implementation period. The facility must comply with the final permit. The statement, "The facility may calculate and record actual emissions on a monthly basis for the first three months after the final permit V-07-008 is issued." was added to Section D.3 compliance

demonstration method b and recordkeeping requirements for the flare in Section B.

33. Miscellaneous Comment, Markup of Typos in Draft Permit Application Package

We have marked up several typographical mistakes in the three documents of the Draft Permit Application Package. We will submit those to the Division in a separate document.

Division's response: The Division has corrected the typographical errors as noted:

Application Summary Form- pages 2 and 3
Permit Statement of Basis- Pages1,2, and 3
Permit- pages 2,3,5,7,8,11,12,13,15, and 16